GEOCHEMISTRY OF OIL SHALES IN EASTERN KENTUCKY

By

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INTRODUCTION

Recent resource assessment studies of eastern Kentucky oil shales have established that this resource is a potential economic synthetic fuel feedstock (1). Extensive geochemical characterization of this resource has been carried out by the Institute for Mining and Minerals Research (University of Kentucky) with support from the Commonwealth of Kentucky Energy Cabinet, the U. S. Department of Energy and private industry. This effort will eventually culminate in the characterization of the entire oil shale resource within the Commonwealth; this particular study addresses the results gained from the first two drilling and sampling phases of the overall effort. The sampling and analysis program was initiated in Lewis and Fleming Counties, Kentucky, resulting in 10 cores being drilled with those core samples being designated as the "K-series" samples in this report. The second phase of the program produced an 11 additional cores in Rowan, Bath, Montgomery, Powell and Estill Counties; these samples are given the "D-series" designation. The location of these core sites as well as current drilling sites are depicted in Figure 1. This paper summarizes the geochemistry of the Devonian and Mississippian age oil shales of the K- and D-series study areas.

GENERAL GEOLOGY AND STRATIGRAPHY

In Kentucky, black shales rich in organic matter (OM) in the Devonian and Mississippian systems crop out in a roughly semi-circular pattern on the flanks of the Lexington Dome. The dome is a structural prominence on the Cincinnati Arch, which stretches between Nashville, Tennessee and southern Ohio. The black-shale outcrops occur in the outer Bluegrass and Knobs from Jefferson and Bullitt Counties on the west to Lewis and Fleming Counties on the east as shown in Figure 1. From the southern end of the semi-circle south into Tennessee, the black shale crops out in river valleys where the overburden is relatively shallow in the Cumberland Saddle, a structural col between the Lexington and Nashville domes on the Cincinnati Arch.

West of the Cincinnati Arch, the black shale dips into the subsurface of the Eastern Interior Basin where it becomes over 450 feet thick in Hardin County, Illinois and Union County, Kentucky (2). On the eastern flank of the Cincinnati Arch, the black shale dips eastward into the Appalachian Basin where it becomes over 1700 feet thick. To the south, the overall section thins to 30 or 40 feet along the crest of the arch.

In each of the three areas described above, the black-shale sequence differs in overall aspect from each of the other areas when viewed in outcrops. This difference has led to three sets of stratigraphic nomenclature having been applied to the black Devonian-Mississippian Shales. The general distribution of the usages of stratigraphic nomenclature is shown in Figure 2.

In eastern Kentucky, the Ohio Shale terminology has been used where the Mississippian Sunbury Shale and the underlying Bedford Shale can still be recognized. A typical stratigraphic section along with down-core carbon distribution is shown in Figure 3. Typically the overburden is a mixture of claystone and siltstone in the Borden Formation. This unit directly overlies the Sunbury Shale which is a black, laminated, siliceous shale rich in organic matter with some pyrite. The Sunbury thins to the south from 20-25 feet in Lewis County to four feet in Estill County.

The Mississippian Sunbury Shale is separated from the underlying OM-rich Devonian Ohio Shale by the Berea Sandstone and Bedford Shale in Lewis County and by the Bedford Shale in the remaining counties. This interburden unit thins to the south from over 100 feet in Lewis County to only a few inches in Estill County. The Ohio Shale is divided into three units as shown in Figure 3. The Cleveland Member is the upper unit. Its lower contact is marked at the upper greenish-gray (OM-deficient) shale of the Three Lick Bed. The lower greenish-gray shale marks the top and the angular unconformity at the base of the black shale, the underlying unit may be the Middle

Devonian Boyle Dolomite, the Silurian Crab Orchard Shale, or the Silurian Bisher Limestone.

The Cleveland Member consists primarily of black to brownish-black laminated siliceous shale. It contains minor amounts of calcareous laminae and cone-in-cone limestone. Pyrite is present as nodules, framboids and irregular forms. Other primary minerals include illite clay and clay- and silt-size quartz.

The Three Lick Bed is a regional stratigraphic marker bed traceable throughout eastern Kentucky, Ohio, West Virginia and Tennessee (3). The bed contains three greenish-gray shales deficient in OM interbedded with two brownish-black, OM-rich shales. The greenish-gray shales contain Lingula, abundant trace fossils and pyritized micro fossils (4, 5).

The lower unit of the Ohio Shale which is present in the outcrop area of eastern Kentucky is the Huron Member. Primarily, the Huron consists of black to brownish-black to gray-black, laminated, siliceous, OM-rich shales. Calcareous laminae, cone-in-cone limestone, dolomitic gray shales, dolomite beds and bioturbated greenish-gray shales occur as interbeds and laminae in the lower parts of the member.

DEFINITION OF ECONOMIC ZONES

For the resource assessment studies, it was necessary to define potentially mineable oil shale zones. The resulting nomenclature has subsequently been carried over into the geochemical studies. For the purposes of the resource assessment, only surface mineable oil shale having an overburden plus interburden to shale ratio of less than 2.5:1 was considered economical. Economic zones were further defined as those resources with greater than 8% carbon (1). In the study area, this included all of the Sunbury shale and a High Grade Zone (HGZ) of the Upper Cleveland Member of the Ohio shale. This zone extends from the top of the member to a depth where the carbon content drops below 8%. This 8% level also corresponds to a point at which the carbon concentration is rapidly decreasing with depth (see Figure 3). A zone of +8% carbon also occurs in the lower Huron, but this oil shale is also high in sulfur, mineral carbon and is separated from the other economic zones by a thick sequence of lean oil shales.

The two defined economic zones (Sunbury shale and the HGZ of the Cleveland Member) are separated by interburden units of the Bedford Shale throughout the study area and the Berea Sandstone in Lewis County. Thickness histograms of the economic zones and their associated interburden units are presented in Figure 4, which shows that the Sunbury Shale decreases in thickness to the south while the Cleveland HGZ remains fairly constant at 25-30' thick. The Bedford and Berea units decrease in thickness rapidly toward the south with less than a foot of interburden separating the two economic zones in Montgomery County.

ORGANIC GEOCHEMISTRY

General

The organic geochemistry of the study samples is summarized by the elemental analysis data in Table I. Extensive detailed data on these samples on a core-by-core basis are available in previous reports (1, 6, 7).

TABLE I

ORGANIC ELEMENTAL ANALYSIS DATA FOR K- AND D-SERIES OIL SHALES

	K-Series				D-Series			
	Sunbury Shale	Cleveland Shale		Huron Shale	Sunbury Shale	Cleveland Shale		Huron Shale
		Total	HGZ			Total	HGZ	
C^a	11.42(3)^b	9.04(2)	11.11(3)	5.61(3)	13.12(10)	9.61(4)	11.08(3)	6.57(15)
H	1.20(4)	.99(2)	1.21(7)	.66(6)	1.47(14)	1.09(5)	1.25(5)	.76(12)
N	.41(5)	.39(4)	.39(3)	.22(7)	.44(10)	.32(10)	.36(10)	.23(16)
S	3.54(8)	2.42(6)	2.51(8)	3.15(3)	3.70(12)	2.79(12)	2.93(10)	3.61(7)

a. Wt % raw shale; H corrected for surface moisture.
b. Numbers in parentheses are coefficients of variation x 100.

Carbon data presented and discussed herein are given as total carbon unless specified otherwise. Mineral carbon contributions from calcite and dolomite are typically insignificant in comparison to total carbon values. Average mineral carbon contents for the K-series stratigraphic units are as follows: Sunbury, 0.01%; Cleveland, 0.06%; and Huron, 0.13%. Comparative data

from the D-series are: Sunbury, 0.14%; Cleveland, 0.10%; and Huron, 0.44%. A general trend toward increasing mineral carbon in the southerly samples of the study area is evident. Distinct calcitic bands in the cores do occur but were removed and analyzed separately and, thus, are not accounted for in the above data.

Hydrogen is present in these shales as surface moisture, mineral-bound hydration water, and organically-bound hydrogen. Surface moisture was determined for each sample; consequently, this hydrogen contribution is corrected for in the presented data. Mineral-bound hydrogen, being difficult to determine directly, is included in the hydrogen data presented. However, positive intercepts of H vs. C plots indicate approximately 0.2 wt% hydrogen from mineral origins. The consistency of these data for general assignment to mineral-bound hydrogen contributions is under current investigation.

Nitrogen occurs almost exclusively as organic nitrogen and N vs. C plots are linear and possess relatively constant slope values indicating a uniform geochemical presence of this element in these shales. Sulfur occurrence in these shales is composed of organic, sulfide and sulfate contributions. Our data indicate that >80% of the sulfur occurs in sulfide minerals, predominantly as pyrite (FeS_2). Current research is aimed at refinement of the sulfur forms data, primarily to assess the organic sulfur content of these shales.

Based on present data, the overall stoichiometry of the raw oil shale organic material is given by the empirical formula $CH_{1.3}N_{031}$. This can be compared to formulas given for western oil shales, e.g. $CA_{1.5}N_{0.032}$ (8) and $CH_{1.7}N_{.027}$ (9). These data indicate that the eastern oil shales of Kentucky are more aromatic in character than the Western oil shales. This characteristic manifests itself in a slight hydrogen deficiency which ultimately limits oil yield. The remarkably similar N/C ratios between the two oil shales is also notable.

Stratigraphic and Regional Trends

Strong stratigraphic trends are evident in the distribution of carbon in the study cores, as Figure 3 illustrates. In general, the carbon content increases from top to bottom in the Sunbury Shale, with carbon values of approximately 9-10% at the top to 15% at the base. This pattern is reversed in the underlying Cleveland Member of the Ohio Shale. The top of the Cleveland has a carbon content similar to the base of the Sunbury, with values decreasing to 4-6% toward its base. The Three Lick Bed of the Ohio Shale shows erratic distribution of carbon, which is as expected, as this unit is defined on the basis of three barren, bioturbated green shales. The pattern of carbon distribution in the Huron Member of the Ohio Shale is the inverse of the Cleveland; the carbon content increases toward the base of this unit, reaching values of 9-10%. This pattern is somewhat broken up by the presence of burrowed and bioturbated green shale intervals toward the base of the Huron.

When the data of Table I are compared, the intra-core organic geochemistry of the individual shale units is relatively consistent considering the variance within each unit. A slight average decrease toward the lower units is evident, however. Intra-core H/C ratios for these data are essentially constant, but slightly higher H/C ratios in the upper Cleveland shales relative to the Sunbury have been observed. Intra-core N/C ratios are generally higher for the leaner Huron Shales; this correspondence has also been noted for Western oil shales (8, 9).

Regional trends in the study area are illustrated for carbon, hydrogen and sulfur in Figure 5. The carbon-hydrogen contents of the Sunbury shale are 11 and 1.1%, respectively, in the northern (Lewis County) cores and peak at 15 and 1.8% in the Powell County core sites before decreasing slightly again toward the south of the study area. The most rapid increase in carbon and hydrogen occurs as this unit thins and may be reflective of slower depositional rates. Regional C-H trends for the Cleveland HGZ are also illustrated but are not as distinct as those of Sunbury Shale. Shale variability as determined by the coefficients of variation in Table I is generally 2-3 times greater for the D-series as compared to the K-series samples. This is accounted for by the greater regional change within the D-series area. Region trends for sulfur generally follow carbon for both units, but levels of the element are noticeably lower in the Cleveland unit relative to the Sunbury.

Organic Geochemistry - Fischer Assay Relationships

Conventional and modified Fischer Assay analyses have been performed on many Sunbury and Cleveland HGZ oil shale samples. The meaning of Fischer Assay results when applied to Eastern U. S. oil shales is somewhat ambiguous. Such results do provide a basis for comparison among the study samples but probably underestimate the amount of extractable oil from the shale and, consequently, do not provide an accurate method for assessing the total recoverable energy from these shales. Comments concerning the applicability of the Fischer Assay test to eastern shales have been made in previous reports by our colleagues (10, 11) and generally indicate that these oil shales are much more sensitive to heating rate, product removal and retort atmosphere variables. Our data also indicate that Fischer Assay data for the same samples among different

performing laboratories is quite variable and is probably indicative of both laboratory and oil shale characteristics.

When the body of Fischer Assay data on the K-series samples is evaluated, mean values for the weighted averages of these cores are 10.3 and 11.9 gal/ton for Sunbury and Cleveland HGZ, respectively. Coefficients of variation of 8.2% (Sunbury) and 6.9% (Cleveland HGZ) were observed with a total range of assay values ranging from 5.4 to 18.4 gals/ton. Current data for some D-series samples are given in Figure 6, which illustrates the Fischer Assay-raw oil shale carbon content relationship for the two oil shale units. It is evident that the Cleveland oil shale yields slightly more oil than the Sunbury oil shale, in spite of the fact that the Sunbury Shale averages more carbon per unit weight. This same relationship was observed for the two oil shale units from the K-series (6) and is assumed to be reflective of kerogen differences between the two oil shales. Correlation of Fischer Assay with hydrogen content yields slightly better correlations indicating again the criticality of the hydrogen content of these shales.

Illustrative Fischer Assay yields and associated oil and gas composition data are presented in Table II for both eastern (29) and western (8) oil shales of nominally similar organic carbon content. The eastern oil shales yield more gas and water and less oil than the western oil shale used for comparison. The major differences in the oil composition include comparatively lower nitrogen and higher sulfur contents for the Sunbury and Cleveland shale oils. The lower H/C ratio for the eastern oils indicate a more aromatic oil, as reported previously (30). Assay contents with less C_3-C_6 and CO_2 contents. The lower C_3-C_6 levels in the case of the eastern oil shales id due to a more efficient condensation of those gases to the liquid product in our assay procedures (10, 11). Gas cleanup would ultimately be expected to yield a higher BTU gas for the eastern oil shale-derived gas than a corresponding western gas due to elimination of H_2S in the former and high CO_2 levels and condensation of much of the C_4-C_6 range in the latter. Finally, it should be emphasized that the compositional information presented is based on Fischer Assay retorting procedures and may not be entirely representative of products produced under commercial scenarios.

INORGANIC GEOCHEMISTRY

Mineralogic Composition

The subject shales are designated silty shales due to their high quartz content. The mineralogic composition of these shales has been studies (12-16) and is summarized in Table III. Illite (2M), muscovite and/or illite/smectite are the predominant clays found in these shales.

Stratigraphic Distribution and Regional Trends

Major and trace element determinations were performed and are presented as weight percent or ppm of the 500°C ash fraction of the samples. This was done to eliminate the effect of variation in organic content and to facilitate comparisons.

When the major element chemistry for the various stratigraphic units are compared, no large differences are found (Table IV). The concentration of Al_2O_3 in the shales is less than what would be expected from a clay shale, which together with the SiO_2 content, substantiates its significant quartz content. The level of K_2O present (about 4%) indicates that the clays are primarily illite or muscovite-mica which agrees with mineralogic determinations made on the shales. The CaO concentration in all of the stratigraphic units is low (generally less than 1.0% (Table IV)), also in agreement with the previous observations made for mineral carbon. Calcium content is generally higher in the Huron, particularly in the D-5 through D-8 cores where the Duffin and Ravenna lithologies are present. There is also a slight geographic trend of increasing CaO concentrations from north to south in the study area.

The coefficients of variation determined among the cores for the major element oxides are generally very low (Table IV) and in many cases almost at the level of analytic uncertainty. Two exceptions to this are CaO and P_2O_5 which are associated with carbonate minerals and phosphate nodules. These are not part of the primary lithologies of the shale and are subject to being either locally abundant or absent.

Unlike the organic elements, the major element chemistry does not show large stratigraphic zonation compared to its lateral continuity. Coefficients of variation for the stratigraphic intervals are only slightly greater than those calculated for the average core data. However, the concentration and distribution of the determined trace elements are stratigraphically controlled. Highest concentrations are found in the Sunbury, followed by the Cleveland and the Huron. The elements which show the greatest zonation based on stratigraphic unit include Mo, Ni, V and Zn. Each of these elements is found to have concentrations in the Sunbury at levels of 2-3 times those of the other units (Table IV). As in the case of the major elements, the coefficients of variation calculated for the trace elements among the cores for the stratigraphic intervals are very low in most cases (Table IV). Unlike the majors, however, the stratigraphic variations are high. This is

reflective of zonation within the individual stratigraphic units.

TABLE II

FISCHER ASSAY YIELDS WITH OIL AND GAS COMPOSITION DATA FOR EASTERN VS WESTERN OIL SHALES

Oil Shale Formation	Sunbury[a]	Cleveland[b]	Green River[c]
Yields			
Oil, gal/ton	14.4	13.4	29.8
Gas, ft[c]/ton	684	740	461
Water, gal/ton	9.8	16.6	3.8
Oil Composition			
C, wt %	83.25	82.41	84.80
H, wt %	10.35	10.11	11.60
N, wt %	0.86	0.77	1.96
S, wt %	2.38	2.75	0.60
Density	0.9197	0.9199	0.9180
Btu/lb	17,800	17,800	18,750[d]
Gas Composition, Vol %			
H_2	37.0	30.6	25.7
CH_4	22.2	24.0	16.5
C_2H_4	1.50	1.60	2.30
C_2H_6	5.98	6.09	6.7
C_3-C_6	4.34	3.88	11.7
CO_2	5.53	7.16	31.1
CO	3.33	4.14	0.7
H_2S	20.4	15.2	1.0
Btu/SCF	743	740	776[d]

a. Data from (29), sample SUN-002, Lewis Co., KY, organic carbon = 13.85%.
b. Data from (29), sample CLE-002, Lewis Co., KY, organic carbon = 14.54%.
c. Data from (8), sample 482B 'B', Anvil Points, CO, organic carbon = 13.61%.
d. Calculated by authors.

TABLE III

MODAL MINERALOGIC COMPOSITION OF DEVONIAN OIL SHALES

	Cleveland (12)	Chattanooga (14-16)
Quartz	30	20-25
Pyrite	5	10-15
Illite	39	
Illite/Muscovite	} 20	} 25-30
Illite/Smectite Mixed Layered		
Kaolinite	Trace	Minor
Chlorite	7	Trace
Carbonates	Minor	Variable
Feldspar	Minor	10
Organics	(on Ash Basis)	15-20

TABLE IV

INORGANIC COMPOSITION FOR K- AND D-SERIES OIL SHALES

| | K-Series | | | | D-Series | | | |
| | Sunbury Shale | Cleveland Shale | | Huron Shale | Sunbury Shale | Cleveland Shale | | Huron Shale |
		Total	HGZ			Total	HGZ	
SiO_2 [a]	63.7(3)[b]	66.6(1)	66.5(1)	64.4(1)	64.18(3)	65.78(1)	66.16(2)	61.93(2)
TiO_2	.8(5)	.9(1)	.8(1)	.9(1)	.76(6)	.85(3)	.82(2)	.85(4)
Al_2O_3	16.7(6)	16.4(1)	16.2(1)	16.6(1)	15.58(2)	15.57(3)	15.15(4)	16.12(4)
Fe_2O_3	8.7(5)	6.8(2)	7.0(3)	7.9(3)	8.12(11)	6.67(4)	6.83(6)	8.20(4)
CaO	.4(28)	.6(21)	.6(20)	.9(29)	.88(114)	.90(36)	.84(43)	1.33(64)
MgO	1.5(6)	1.3(3)	1.4(2)	1.3(5)	1.43(4)	1.37(5)	1.36(5)	1.78(22)
K_2O	4.4(7)	4.3(1)	4.2(2)	4.3(1)	4.11(3)	4.13(3)	4.08(3)	4.26(3)
Na_2O	.4(20)	.5(13)	.5(13)	.5(8)	.38(19)	.50(15)	.47(18)	.54(11)
P_2O_5	ND	ND	ND	ND	.29(77)	.22(44)	.28(48)	.12(23)
Ba[c]	645(4)	619(3)	607(4)	633(3)	622(7)	570(4)	568(4)	564(5)
Co	24(3)	21(2)	20(2)	25(2)	24(6)	19(3)	19(4)	27(3)
Cr	200(3)	159(2)	195(4)	90(1)	175(10)	151(19)	185(4)	93(4)
Cu	113(3)	91(3)	111(4)	57(3)	134(9)	97(6)	114(5)	74(20)
Mo	281(5)	94(3)	89(8)	66(5)	248(15)	104(4)	92(7)	86(6)
Ni	272(3)	125(9)	141(2)	81(3)	288(14)	129(4)	139(3)	96(13)
V	1533(5)	760(5)	1024(5)	209(3)	1155(24)	677(4)	796(6)	216(5)
Zn	1126(6)	444(5)	622(7)	144(8)	1202(15)	412(8)	510(7)	173(9)
U	37(5)	20(7)	20(7)	ND	43(15)	21(4)	19(4)	22(6)

a. Wt % in 500°C Ash
b. Coefficients of variation x 100
c. ppm (wt) in 500°C Ash

     The concentrations of certain trace elements also appear to show regional trends. As an example of these trends, Figure 7 presents the regional distribution of Mo, Ni, V and Zn. Each of these elements shows a slight overall decrease in concentration between Lewis County (K-9 or 8) in the north and Estill County (D-10) in the south for both the Sunbury and the Cleveland HGZ. However, the regional trends for the Sunbury are somewhat obscured by an increase in concentration for Mo, Ni and Zn and a decrease in concentration for V in the region between Montgomery and Powell Counties. The cause for these regional anomalies is presently unclear.

Trace Metal Affinites

     Trace-element and major-element associations in the oil shales have been a subject of several studies (17, 18). In general, the trace elements can be divided into three groups: those which have an affinity for carbon (Cu, Cr, Ni, V), those which have an affinity for sulfur (Co, Zn), and those which have an affinity for the silicates and carbonates (Ba) (not reported here). The associations are also, to some degree, stratigraphically dependent. For example, in Lewis and Fleming Counties, Cr, Ni and V concentrations were found to be strongly correlated with carbon concentration (correlation coefficients = .95, .91 and .82, respectively) in the shales of the Cleveland Member, but not strongly correlated in the Huron and Sunbury (18). Zn is listed as having an affinity for sulfur, even though it did not have a significant correlation. It is often associated with its own mineral phase (sphalerite, ZnS) and the lack of correlations with total sulfur is not surprising. Correlation coefficients for the trace metal affinities found in the K-series is presented in Table V. The trace element affinities discussed are similar to the observations of Keogh (19) who studied the trace element chemistry of the organic matter separated from the shale.

Economic Implications of Trace Element Geochemistry

     The regional trends in the stratigraphy and geochemistry of the defined economic units are relevant to mining, processing and by-product recovery potential. Trace metal data for the total economic zone are presented in Table VI; these data are weighted for the thickness of the Cleveland HGZ and Sunbury Shale and, therefore, are representative of potential feedstocks for a retorting system.

     The high concentration of metals in the eastern oil shales has led to considerable

speculation concerning the potential for by-product metals recovery (20-24). Much of this interest has centered on the recovery of such metals as Mo, V, Ni, Cu, U, Th, and Al. At present, the potential for the recovery of these metals appears to be sub-economic (1).

TABLE V

CORRELATION COEFFICIENTS FOR METALS AFFINITIES OF EASTERN SHALES

Element	Lithologic Unit	K-Series Data Carbon	Sulfur
Co	Sunbury	-.38	.85
	Cleveland	.23	.76
	Huron	.67	.90
Cr	Sunbury	.17	-.34
	Cleveland	.95	.51
	Huron	-.45	-.55
Cu	Sunbury	.81	-.12
	Cleveland	.95	.44
	Huron	.54	.49
Mo	Sunbury	.15	.08
	Cleveland	.11	-.12
	Huron	.90	.78
Ni	Sunbury	.40	.25
	Cleveland	.91	.37
	Huron	.40	.17
V	Sunbury	.07	.15
	Cleveland	.82	.10
	Huron	.01	-.17

Underlined coefficients considered significant.

TABLE VI

TRACE METAL CONTENT OF TOTAL ECONOMIC ZONES

	K-9 Lewis County	K-4 Fleming County	D-1 Rowan County	D-4 Bath County	D-6 Montgomery County	D-8 Powell County	D-10 Estill County	Study Area Mean
Mo	158	151	175	152	145	119	99	148
Ni	191	187	187	172	184	172	153	179
V	1226	1164	1058	911	891	795	738	1025
Zn	819	749	728	663	698	636	545	723

Several of the metals present in eastern oil shales are of importance from a processing standpoint, however. Certain elements, particularly those shown to be associated with carbon (Table V) may tend to concentrate in the oils produced during retorting. Of particular concern in process and oil upgrading are As, V and Ni. These elements are known to be a problem in upgrading oils due to cracking and reforming catalyst poisoning. During upgrading, these oils require processing to remove these elements. The high trace element concentrations of Ni and V in the eastern oil shales (Tables IV and VI) coupled with their organic affinity imply that they may partition to the oils during retorting. Although the As values for these oil shales are limited, preliminary data for the units are: Sunbury (5-300 ppm), Cleveland (1-80 ppm) and Huron (30-50 ppm). Arsenic also is expected to concentrate in the oils during retorting. These predictions are somewhat confirmed by preliminary data presented in Table VII for a single two stage retort produced oil (25). The metals composition of other crude oils are also presented for comparison.

TABLE VII

TRACE ELEMENT COMPOSITION OF AN EASTERN SHALE OIL (CHATTANOOGA),
A WESTERN SHALE OIL AND TWO PETROLEUM CRUDES

	Chattanooga 1st Stage (25)	2nd Stage (25)	Paraho (25)	Alberta Canada Devonian Crude (26)	Venezuelan Crude (27)	Nigerian Crude (28)	Iranian Crude (28)	California Terhasy Heavy Crude (27)
As (ppm)	50	59	28	.111	.005	1.2	.095	.66
Ni (ppm)	5.0	5.9	1.8	9.4	117	5.9	12	94
V (ppm)	6.3	6.3	.2	13.6	1120	9.5	53	7.5

CONCLUSIONS

The principal form of carbon present in the oil shale is as organic matter. Mineral-bound carbon was found to be insignificant, with the exception of the Duffin zone, a localized dolomitic lithology present near the base of the Huron.

Carbon and hydrogen are strongly zoned stratigraphically, with highest levels present in the upper and lower portions of the oil shale section. The variability of the organic chemistry among the study cores is low in comparison.

The Fischer Assay yields of the two economic units were similar, averaging 10.3 gal/ton for the Sunbury shale and 11.9 gal/ton for the Cleveland HGZ. The Fischer Assay data underestimates the maximum potential oil yield of these shales, however.

The major element chemistry is found to be both stratigraphically and laterally consistent for the oil shales.

Trace element concentrations are found to be highest in the Sunbury Shale, followed by the Cleveland and Huron members of the Ohio Shale. Trace element concentrations were found to be strongly stratigraphically zoned, but relatively consistent, among the cores.

The major regional trends affecting mining, processing and by-product recovery (north to south and including Lewis and Fleming Counties) include:

1. the thinning and virtual disappearance of the stratigraphic intervals separating the Sunbury Shale and Cleveland HGZ;

2. the thinning of the Sunbury Shale;

3. an increase in carbon and hydrogen in the Sunbury Shale (concommitant with thinning); and

4. a decrease in trace element content for the total defined economic zone.

Trace elements exhibited three types of association: those having an affinity for carbon (Cu, Cr, Ni, V), those having an affinity for sulfur (Co, Zn) and those having a silicate and/or carbonate affinity (Ba).

Trace elements, particularly those associated with the oil shale kerogen, may be incorporated into the oil product and present subsequent processing problems.

ACKNOWLEDGMENTS

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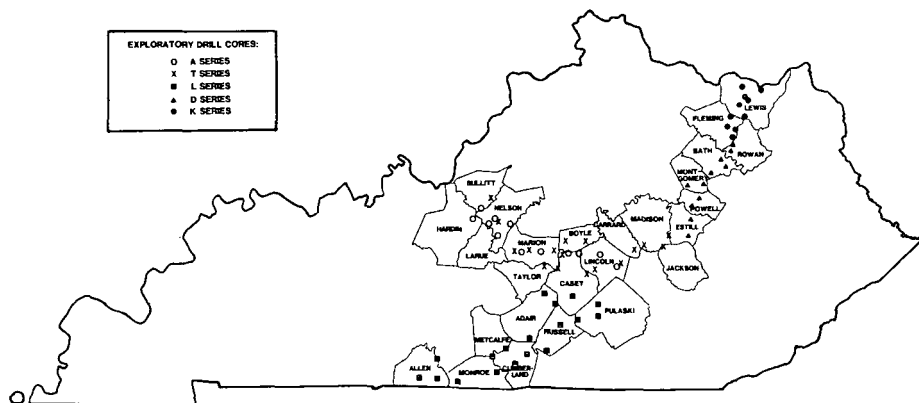
Figure 1. Depiction of oil shale resource exploration core sites in Kentucky. Devonian and Mississippian oil shales outcrop in the counties indicated. Drill cores designated as K- and D-series are the subject of this report.
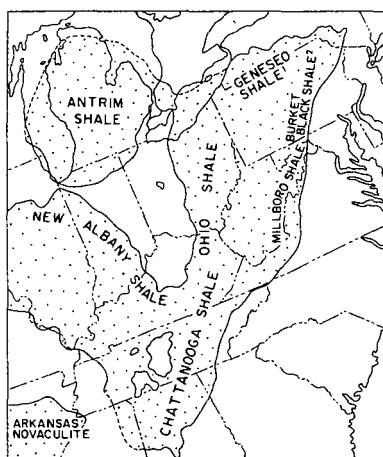

Figure 2. Geographic distribution of Devonian-Mississippian oil shale in the Eastern United States.

BORDEN FORMATION
most important for study are the Nancy and Farmers Members and Henley Bed. Nancy Member is a gray to greenish-gray clay shale. 100-200' thick. Underlying Farmers Member is a light-gray to yellow siltstone with interbeds of silty shale 20-80' thick. The Henley Bed is a greenish-gray to gray glauconitic shale 7.5-26.8' in thickness in study cores.

SUNBURY SHALE   Finely laminated black shale with small intervals of brownish-black.
13.3-18.4' thick in cores, common pyrite bands and nodules, sparsely fossiliferous.

BEREA SANDSTONE   Light-gray siltstones and sandy siltstones with interbedded medium to dark-gray shales, becoming more shaley toward the base. Contact with underlying Bedford chosen at the point where shale/siltstone content is equal. Zero to seventy five feet thick in study cores. Pyrite blebs and nodules common.

BEDFORD SHALE   Medium to dark-gray shale interbedded with light-gray siltstones. Unit is generally silty towards the top. Pyrite bands and nodules, common to abundant, scattered siderite nodules also present. Thickness ranged from 25-68' in study cores. Decreasing in thickness from north to south in Lewis and Fleming counties. Sparsely fossiliferous.

CLEVELAND MEMBER   Black to brownish black shale in upper part to olive-black to brownish-gray shale in lower part. Pyrite blebs, stringers and bands, phosphate nodules and thin calcisiltite bands are common. Linguloid brachiopods and Tasmanites are common fossils. Thickness from 49.9-65.0' in study cores.

THREE-LICK BED   Unit consists of three greenish-gray bioturbated shales separated by two black shale beds. Pyrite, present as infilling in burrows and calcisiltite bands are found. 19.6-11.6' thick in study cores.

HURON MEMBER   Brownish-black to gray-black to brownish-gray shale, also containing intervals of burrowed and bioturbated greenish-gray shales. These intervals are abundant toward base of the unit. Vitrain bands and all forms of pyrite are present, calcisiltite laminae and bands are abundant. Tasmanites, Foerstia and linguloid and orbiculoid brachiopods are common fossils in this unit. Thickness in cores ranged from 208.3-127.8', generally decreasing from north to south in study area. A regional unconformity occurs at the base of the Huron.

OHIO SHALE

BISHER LIMESTONE   Sandy stylolitic gray to yellowish-gray dolomite. Commonly vuggy with petroleum stained or filled vugs. Highly variable in thickness. Ranging from 0-100', generally thicker to north in study area.
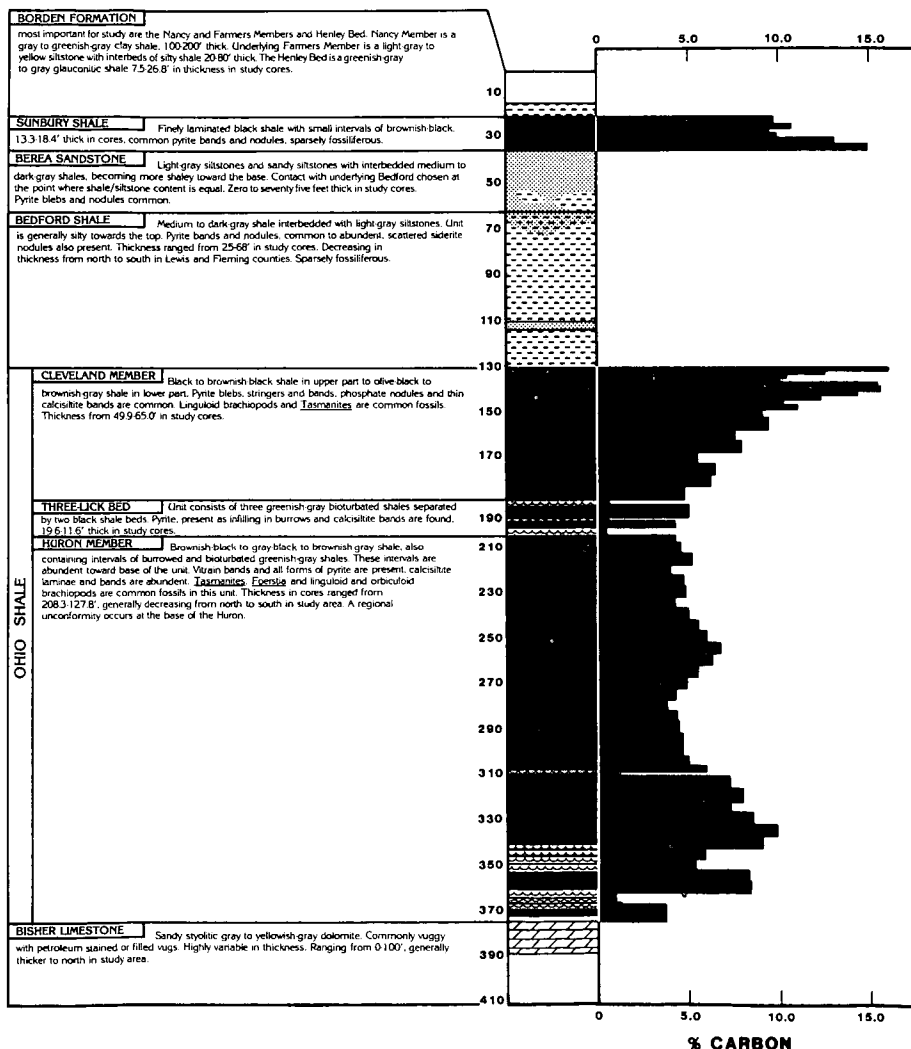
% CARBON

Figure 3. General stratigraphic column for the Devonian-Mississippian black shales in Eastern Kentucky.
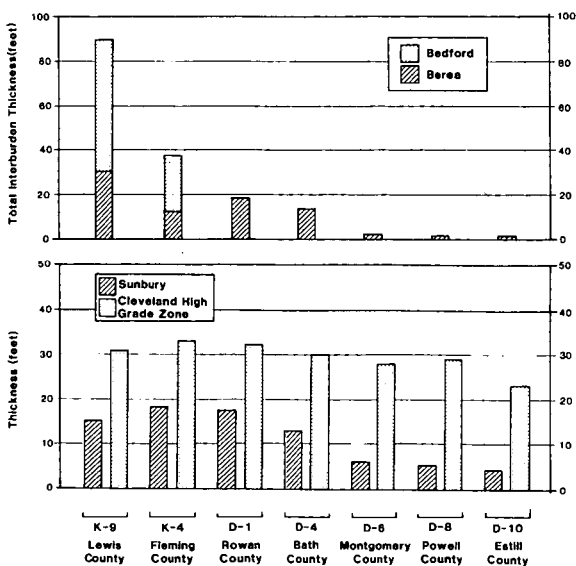
Figure 4. Thicknesses of economic oil shale units and their associated
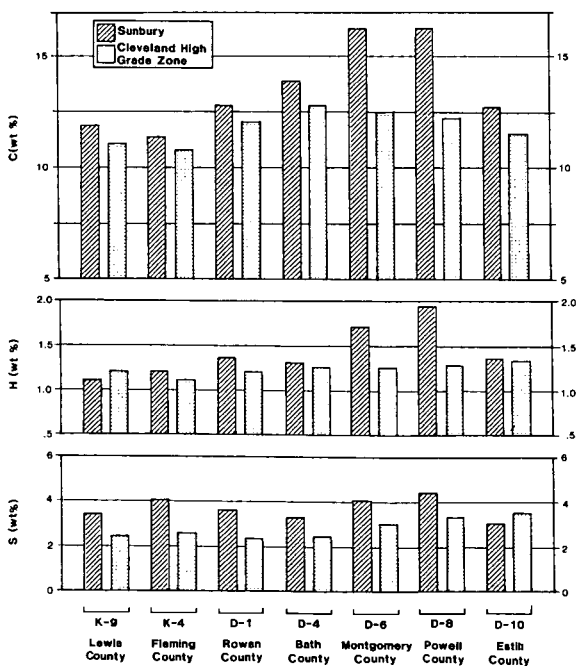interburden units for selected cores in study area.

Figure 5. Regional trends for carbon, hydrogen, and
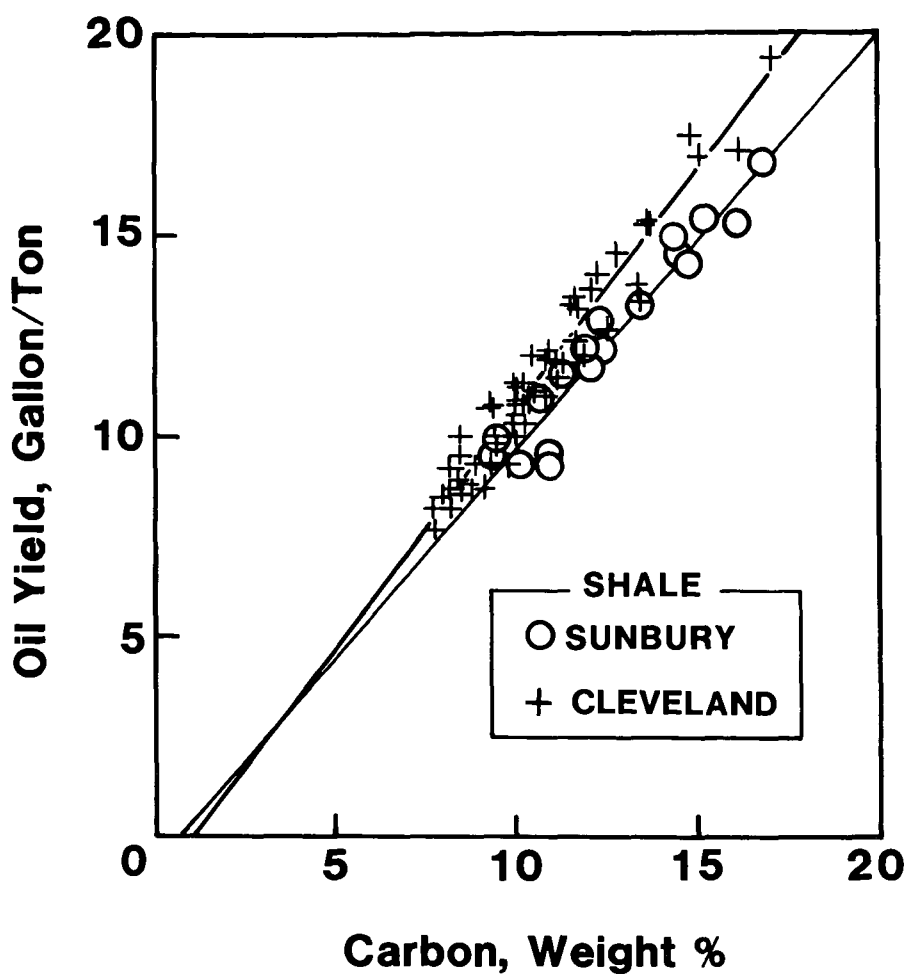sulfur in selected cores of study area.

Figure 6. Plot of Fischer Assay yields and carbon content for D-series oil shales. Regression data are:

Sunbury Shale: Oil yield = 1.03 (%C) - 0.69 (r = .97)

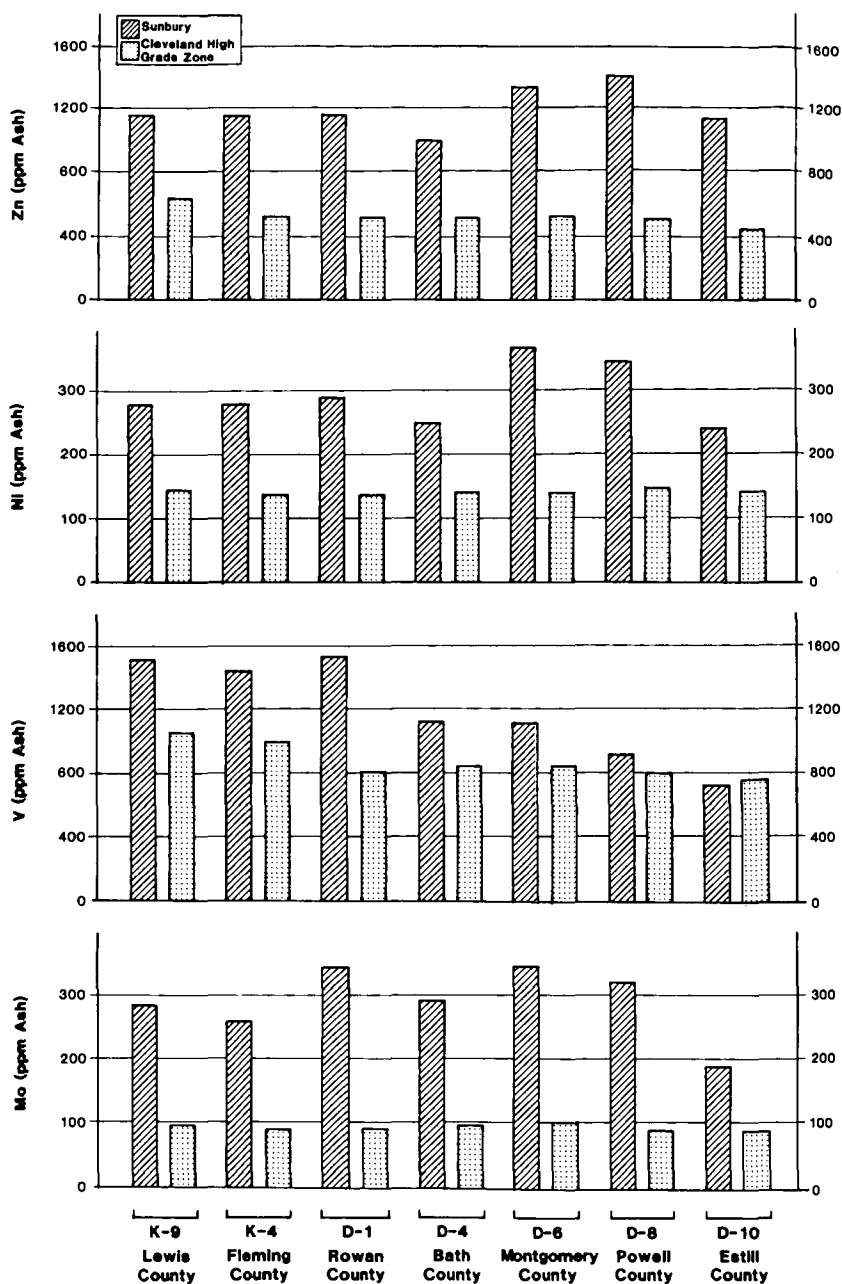Cleveland Shale: Oil yield = 1.18 (%C) - 1.16 (r = .97)

Figure 7. Regional trends for certain trace elements
in selected cores of study area.